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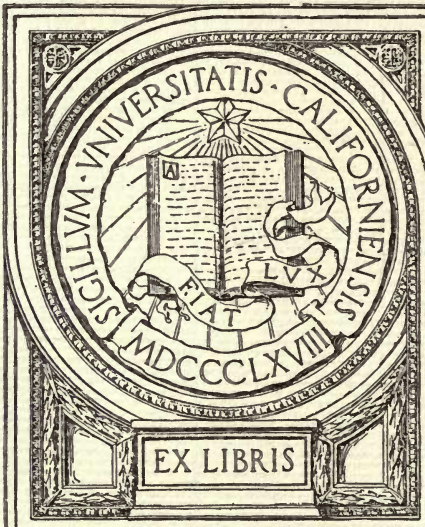
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A Study of the Vapor Pressures of Potassium Compounds, with Applications to the Recovery of Potash by Volatilization

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE COLUMBIA UNIVERSITY, IN THE CITY OF NEW YORK

BY

Jerome John Morgan, B.S., M.S.

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NEW YORK CITY

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ACKNOWLEDGMENT

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Measurement of Vapor Pressures of Certain Potassium Compounds

Anderson and Nestell,[1]* in a report on "The Volatilization of Potash from Cement Materials," give the predominating factors affecting the recovery of potash in the furnace gases beyond the furnace, as follows:

(1) The temperature prevailing in the kiln; (2) volume of gas passing; (3) the intimacy of contact between the furnace gases and the cement mix; (4) the vapor pressure of the potash salt or salts formed; (5) the possibility of dissociation under certain furnace conditions (oxidizing, neutral, or reducing atmosphere or changing temperature) to components of greater or less volatility than the original salt; (6) the degree of saturation of the gas in contact with the cement material; (7) the rate of diffusion both of the salt vaporizing in the interstices of the cement mix to the surface of contact with the gas stream, and of the saturated gas at the surface to the leaner gas areas beyond.

Of these seven factors, all may be more or less varied at will except the fourth, namely, *the vapor pressure of the potash salt or salts formed.* It was decided, therefore, that the fundamental thing in a study of the volatilization of potash is the determination of the vapor pressure of the potassium compounds involved. In the present work results of vapor pressure measurements are given for three natural silicates, leucite, orthoclase feldspar, and glauconite, which are sufficiently abundant to serve as sources of potash, and for four other potassium compounds, the chloride, carbonate, hydroxide, and sulfate, which are of particular interest on account of their connection with the recovery of potash from cement mill flue dust. The knowledge acquired in these vapor pressure measurements will later be applied to the study of the volatilization of potash from mixtures of silicates with releasing and volatilizing agents.

PREVIOUS WORK

In 1866, Bunsen[2] determined the relative volatility of certain salts by heating a centigram bead of the

* Numbers refer to references on page 26.

salt on a platinum wire in the hottest part of a Bunsen flame and measuring the time required for the salt to volatilize. In 1897, Norton and Roth[3] repeated and extended the work of Bunsen. The volatility of sodium chloride thus measured in each case was taken as unity. The results of these investigators, as far as they relate to potassium compounds, are given in Table I.

TABLE I—VOLATILITY OF POTASSIUM COMPOUNDS, TAKING THE VOLATILITY OF SODIUM CHLORIDE AS UNITY

COMPOUND	Results of Bunsen	Results of Norton and Roth
Iodide	2.828	2.362
Bromide	2.055	1.860
Chloride	1.288	1.083
Fluoride	...	0.329
Carbonate	0.310	0.277
Sulfate	0.127	0.149

Bergstrom,[4] in 1915, found the boiling points of the potassium halides to be as follows: potassium chloride 1500°, potassium bromide 1435°, and potassium iodide 1420°. Niggli[5] found that a mixture of potassium carbonate and silica heated for 60 hrs. at 900° to 1000° lost 15 mg. of K_2O. In addition, many of the recent articles dealing with processes for recovering potash from silicates contain statements as to the relative volatility of certain potassium compounds, but, with the exception of the work of Anderson and Nestell,[1] it is believed that there has been no previous quantitative study on the volatilization of potassium compounds.

METHOD OF VAPOR PRESSURE DETERMINATION

On account of the difficulty of finding a gastight material which would withstand the corrosive action of potassium compounds at high temperatures, and of measuring small pressures at these temperatures, it seemed useless to attempt to employ a static method for measuring the vapor pressure. Hence the dynamic method of von Wartenberg[6] was chosen.

In this method a measured volume of gas is passed over a weighed quantity of the substance whose vapor pressure is to be determined at the desired temperature. The amount volatilized is found by the loss of weight, and the partial pressure is calculated from the relation:

$$\text{Pressure of substance} = \frac{\text{Moles of substance} \times \text{total pressure}}{\text{Moles of gas} + \text{moles of substance}}$$

This partial pressure of the volatilized substance represents its vapor pressure only if the gas passed over the heated substance is saturated with the vapor of

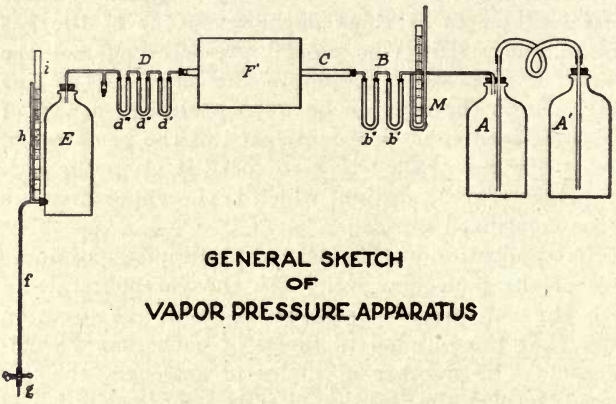
the substance at the given temperature, a condition which is never realized experimentally. However, the degree of saturation of the gas stream is inversely proportional to its speed. Hence by determining these partial pressures at three or more speeds of the gas stream, and plotting the partial pressures against the speeds, it is possible to obtain the slope of the line which shows the relation between partial pressures of the volatilized substance and speed of the gas stream. If this line is extended to zero speed it gives the partial pressure at saturation, which is the vapor pressure of the volatilized substance.

The application of this method presupposes a knowledge of the molecular weight in the gaseous state of both the substance volatilized and the gas used, in order that the number of moles of each may be calculated. The number of moles of nitrogen, the gas passed through the reaction chamber, was easily found by weighing the water displaced by the nitrogen at a given temperature and pressure. In the case of the potassium compounds volatilized, the density in the gaseous state has been determined for only one of the compounds studied. Nernst[7] has shown that the molecular weight of potassium chloride at high temperatures corresponds to the simple formula KCl. In calculating the vapor pressures of the other compounds it was necessary to make certain assumptions regarding the molecular weight of the compound volatilized. The details of these assumptions are given under the discussion of the results for each compound. It can be pointed out here, however, that should later work show that the assumed molecular weight in any case is wrong, it will simply necessitate recalculation of the results and will not impair the usefulness of the experimental data. Furthermore, a vapor pressure here given, used in connection with the assumed molecular weight, will give practically the same result in calculation of the amount of potash necessary to saturate a given volume of gas at a given temperature and pressure as would a corrected molecular weight used with the recalculated vapor pressure. Nevertheless, to avoid misunderstanding special attention is called to the fact that, with the exception of the value for potassium chloride, the vapor pressures herein reported are based upon assumed molecular weights.

VAPOR PRESSURE APPARATUS

A general sketch of the apparatus is given in Fig. 1.

It consisted of the gas container A, the purifying train B, the vapor pressure tube C, which was heated in an electric furnace, F, the absorbing train D, and the gas measuring apparatus E.



GENERAL SKETCH
OF
VAPOR PRESSURE APPARATUS

FIG. 1

The gas, nitrogen, which was to be passed through the vapor pressure tube was contained over water in a large bottle, A, which was connected by a syphon with another bottle, A′, containing a supply of water. This second bottle was suspended from a screw elevator so that the pressure of the gas in the apparatus could be kept constant within one centimeter of water pressure during the course of an experiment. A small manometer, M, filled with water showed the pressure in the apparatus.

After leaving the gas container and before entering the vapor pressure tube the gas was freed from any carbon dioxide which might be present by passing through the soda lime tube *b′*, and dried by passing through the calcium chloride tube *b″*, of the purifying train B.

After leaving the vapor pressure tube the gas passed through the absorbing train D, which consisted of three U-tubes filled as follows: *d′*, granular anhydrous calcium chloride; *d″*, soda lime in the first leg and bend and calcium chloride in the second leg; *d‴*, calcium chloride. The object of this purifying train was to prevent moisture from diffusing back into the vapor pressure tube and to absorb for weighing carbon dioxide set free by heating potassium carbonate in the determination of its vapor pressure.

The speed at which the gas was passed through the vapor pressure tube was regulated by the size of the capillary in the tip *g*, through which water was allowed

to flow from the bottle E, and the volume of gas passed through the vapor pressure tube was determined by weighing the water displaced. By using a bottle with large cross-section and extending the outlet tube *f*, 2 liters of gas could be drawn into the measuring apparatus with a loss of only about 3 in. in a total head of 40 in. This is a change of 7.5 per cent, but experiments with different sizes of capillary tips showed an extreme variation of about 6 per cent in the speed of the water flowing during the first minute and during the last minute. The speed of the gas stream, therefore, varied during the course of an experiment not more than 3 per cent from the mean speed. The tube *h*, connected with the outlet tube, was open at the top and allowed the pressure in the measuring apparatus to be read upon the scale *i*. The rubber stopper of the bottle E had four holes and carried, besides the inlet tube shown in the figure, a tube by which water could be introduced and two thermometers, one to show the temperature of the gas and the other that of the water. In order to give as small variation as possible in the speed of the gas stream, before beginning an experiment a weighed quantity of water was run out and the level of the water brought below the shoulder of the bottle. The temperature of the gas at the beginning and end of the experiment was noted and correction made whenever necessary for the change of volume due to change of temperature.

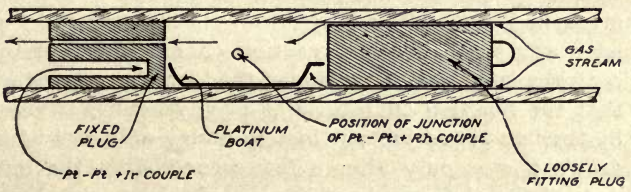


FIG. 2—LONGITUDINAL SECTION OF CENTRAL PORTION OF VAPOR PRESSURE TUBE

A longitudinal section of the vapor pressure tube C is shown in Fig. 2. The tube was made of "Impervite" porcelain, 24 in. long and 1 in. bore, with walls about three-sixteenths inch thick. It was glazed on the outside and was found to be gastight at the temperatures employed. Into this tube was cemented with a grout of impervite body the fixed plug of impervite which was perforated with a one-sixteenth inch hole and had a recess for the Pt — Pt + Ir thermocouple as shown. The loosely fitting plug was also

of impervite body, unglazed, and had embedded in it a piece of platinum wire by which it could be withdrawn from the tube. The diameter of this plug was about one-sixteenth inch less than the internal diameter of the tube. Gas flowing through the vapor pressure tube was heated by passing through the space between the loosely fitting plug and the walls of the tube, and after passing over the substance contained in the platinum boat and taking up its load of vapor left the reaction chamber by the one-sixteenth inch hole in the fixed plug. The entrance end of the tube, which projected about 7 in. from the furnace, was closed by a rubber stopper carrying a glass tube through which the gas was introduced. The exit end of the vapor pressure tube, which projected from the furnace only about 1 in., was closed by a special stopper molded of a mixture of portland cement and asbestos. This was doubly perforated and carried an exit tube for the gas and a double-bored porcelain protecting tube for the platinum-iridium thermocouple. It was cemented into the tube by a mixture of sodium silicate and barium sulfate, and the joints were made gastight by coating with Bakelite varnish. At the higher temperatures the ends of the vapor pressure tube were cooled by strips of wet filter paper so that there was no decomposition of the rubber stopper or of the Bakelite varnish.

The vapor pressure tube was heated in a molybdenum-wound electric furnace, details of which are given in Fig. 3. The position of the tube in the furnace was such that the reaction chamber was in the central evenly heated portion of the furnace. Evidence that the reaction chamber was evenly heated is given by the fact that when the loosely fitting plug was withdrawn it was only after a few seconds that the outlines of the platinum boat became visible.

The temperature of the furnace was regulated by suitable resistances and was controlled by means of a platinum-iridium thermocouple connected with a Siemens and Halske millivoltmeter. The hot junction of the thermocouple was located in the recess in the fixed plug as shown in Figs. 2 and 3. The cold junction connections of the couple wires with the copper leads of the millivoltmeter were made in mercury, which was kept at a constant temperature by a water bath. The temperatures in the reaction chamber corresponding to readings on the millivoltmeter were determined at the beginning of each set of experiments

by a platinum-rhodium couple and a Leeds and Northrup service potentiometer.

By substituting for the regular loosely fitting plug a perforated plug of the same size, the hot junction of the platinum-rhodium couple was supported over the empty platinum boat in the position indicated in Fig. 2. Gas was then run through the vapor pressure tube just as in a regular experiment. The cold junction connections of the platinum-rhodium couple with the leads of the service potentiometer were silver soldered and kept at 0° C. in a vacuum bottle packed with ice. The temperature was calculated from the electromotive force read on the potentiometer by Holman's formula,

$$e = mT^n,$$

using the values $m = 0.00275$ and $n = 1.18$, which were obtained for this particular thermocouple by calibration against the freezing points of zinc, antimony, and copper, by Mr. Roland P. Soule in the physics department of Columbia University. It is thought that these temperatures are correct within ±10° C., and the variation of the temperature during the course of an experiment was always well within these limits.

PROCEDURE

When the temperature in the tube, as shown by the platinum-iridium couple, had become constant at the required point, and a constant pressure of about 2 cm. of water showed that there was no leak in the system, the loosely fitting plug was withdrawn, a platinum boat containing a weighed amount of potassium salt was introduced, the plug quickly replaced, and the gas stream through the tube started by allowing water to run from the capillary tip *g* (Fig. 1) into a weighed container. The temperature in the tube was read at 3- to 5-min. intervals, and kept constant within ±5°; the pressure in the system was kept constant within ±0.5 cm. of water by raising the syphon bottle of the gas container. After about 2 liters of gas had been drawn through the tube the gas stream was interrupted and the boat containing the potassium salt quickly removed.

The time between starting and stopping the gas stream was noted, as well as the temperature of the gas in the measuring apparatus and the pressure in the apparatus. The volume of gas at this temperature and pressure and saturated with water vapor was found by weighing the water displaced, its volume

under standard conditions and dry was calculated, and from this the number of moles of gas passed through the vapor pressure tube was determined. The amount of potassium compound volatilized was found either by loss of weight or by analysis. All weighings were

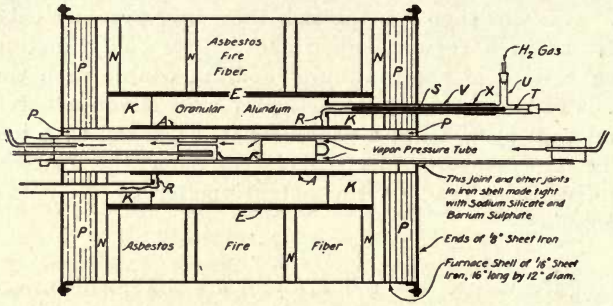


FIG. 3—SECTION OF MOLYBDENUM-WOUND ELECTRIC FURNACE

A—Alundum Core, 10" × 2" Bore, Wound with 27 Ft. 0.028" Molybdenum Wire
E—Alundum Core, 12" × 5" Bore
K—Alundum Cement Rings
N—Rings of 1/2" Asbestos Wood
P—Asbestos Fire Felt, 1/4" Thick
R—Leads of Molybdenum Wire, 4-Ply
S—Electric Connector of 5/16" Steel Rod
T—No. 10, Copper Feed Wire
U—Glass "T" Tube
V—Porcelain Insulating Tube
X—Rubber Tubing

corrected to actual grams mass, and the total pressure, as read from the water manometer and a barometer, was reduced to millimeters of mercury at 0° C.

PROBABLE ERRORS

The sources and magnitudes of the errors in the vapor pressures of potassium chloride determined by this method may be classified as follows:

(1) Errors in measuring and controlling the temperature in the vapor pressure tube. It is believed that the temperature in the vapor pressure tube was determined correctly within ±10°, and that the variation of temperature during the course of an experiment was well within these limits. The maximum magnitude of these errors, therefore, varies from 9 per cent at 1044°, where a change of 10° in temperature makes a difference of 2.14 mm. in a total vapor pressure of 24.1 mm. of mercury, to 13 per cent at 801°, where a variation of 10° changes the vapor pressure 0.205 mm. in a total of 1.54 mm.

(2) Errors in determining the volume of gas passed through the vapor pressure tube. These errors may be due to (*a*) leaks in the system, (*b*) changes in temperature and pressure during the experiment, (*c*) inaccuracy in finding the amount of water displaced. The errors due to leaks in the system were carefully guarded against and are believed to be absent or at least negligible. Those due to changes in temperature of the gas in the measuring apparatus were always less than 0.5 per cent, and

those due to changes in pressure not more than 0.2 per cent. The error in weighing the water displaced was 0.1 per cent, or less.

(3) Errors in determining the amount of potassium chloride volatilized varied from less than 0.2 per cent at 1044°, where the error was not more than 0.1 or 0.2 mg. in weighing and the amount lost by volatilization was from 110.0 to 131.3 mg., to 3 or 4 per cent at 801°, where the amount volatilized was 5.4 to 7.8 mg.

(4) Errors due to volatilization of the potassium compound while the boat was being placed in and removed from the tube. This error was never greater than the error in weighing, for whenever it was evident that a weighable amount of the potassium salt was being lost in this manner the amount was found by blank determinations and a correction applied. Hence this error is included in the errors in weighing.

(5) Excess volatilization of the potassium compound due to back diffusion of the vapor against the gas stream and condensation on cooler portions of the tube and plug in front of the vapor pressure chamber. The magnitude of this error is hard to estimate. It was kept small by having the loosely fitting plug fit as tightly as possible and still allow for rapid removal and replacement, and by increasing the velocity of the gas stream whenever it became evident that the back diffusion was causing material error. It is this error which limits the application of the method to vapor pressures under 25 or 30 mm., on account of the difficulty of working with gas-stream speeds above 200 cc. per minute. It is believed that the amount of this error is never greater than the extreme variation of a single determination from the mean straight line used in extrapolating, which is never over 5 per cent.

(6) Low volatilization due to partial saturation of the gas with potassium compounds volatilized from condensations in the tube during previous experiments. To avoid this error as far as possible, air was passed through the tube for some time between experiments. If allowed to accumulate, these condensations became a serious source of error, and when it became evident that they were seriously interfering, the tube was flushed out with air while heated at a temperature considerably higher than that at which the experiments were to be run, or else a new tube and new plugs were used. Owing to these precautions and the fact that this error is somewhat compensated for by the back diffusion mentioned in (5), it is thought that the magnitude of this error is never over 5 per cent.

(7) Errors due to uneven distribution of the vapor of the potassium compound in the gas stream over the boat. The direction and magnitude of these errors is difficult to estimate. Their presence was shown in some of the preliminary work on potassium chloride, where it was found impossible to get duplicates that checked using two different platinum boats, one of which happened to be deeper and narrower at the top than the other. The results using the narrow boat were invariably lower

than those with the wider boat, due to the fact that a pocket of stagnant saturated gas was formed in the top of the narrow boat and hindered evaporation of the potassium compound. In the determinations reported, shallow wide boats were used and closely agreeing duplicates were obtained. It is believed that under these conditions the errors of this class are not serious.

(8) Errors due to reaction of the potassium chloride vapors with the impervite tube and plugs. Undoubtedly there was some reaction between the vapors and the material of which the tube and plugs were made, and this would tend to absorb the potassium chloride vapors and give high results. However, on account of the rapidity of the gas stream and the very small amount of vapor present in the gas, it is thought that the error due to this cause is entirely negligible.

(9) Errors in extrapolation. The partial pressures were plotted against the speeds of the gas stream on coördinate paper, and the straight line which agreed with the greatest number of points was extended to zero speed. To check the accuracy of this graphic method, the equations for the lines through pairs of mean results for different speeds were written and solved for the pressure (x) at zero speed ($y = 0$). The mean of the pressures thus found, which agreed very closely with the pressure found by the graphic method, was taken as the vapor pressure at the temperature in question. The extreme variation of the pressure values thus calculated from the mean value was about ± 10 per cent, and it is believed that the vapor pressures here reported are reliable within these limits.

VAPOR PRESSURE OF POTASSIUM CHLORIDE

It has been shown by Nernst[7] that the vapor density of potassium chloride corresponds to the simple formula KCl. Hence in determining the vapor pressure of this compound the amount volatilized can be found directly by loss of weight. The salt used was from a 2-lb. bottle of J. T. Baker Chemical Company's C. P. Analyzed Potassium Chloride. According to the label it contained 0.001 per cent or less of each of the following impurities: iron, calcium oxide, magnesium oxide, and sulfuric anhydride, and also a trace of sodium. Qualitative tests for the above impurities showed that they were present only in extremely minute quantities. To expel moisture and avoid mechanical loss from decrepitation, the salt before being weighed for analysis or for use in a vapor pressure determination was fused in a weighed platinum boat. The total potassium present was determined both by the perchloric acid method, which separates any sodium which might be present, and by evaporating a weighed portion of the fused chloride with an excess of sulfuric acid in a platinum dish, igniting to constant weight and weighing as potassium sulfate. The results cal-

culated as potassium chloride by the perchlorate method were 100.10 and 100.05 per cent, and by the sulfate method, 99.98 and 99.94 per cent. It is safe to conclude, therefore, that the fused salt is practically pure KCl. Anaylses of the residues from the platinum boat after vapor pressure determinations showed that these also were pure potassium chloride. The potassium chloride left in the boat after Expts. 58 to 63, inclusive, weighed 0.2040 g., and yielded 0.2387 g. of potassium sulfate, which is equivalent to 0.2042 g. KCl; the residue from Expts. 67 to 71 weighing 0.5980g., gave 0.6990 g. of K_2SO_4, equivalent to 0.5981g. of KCl

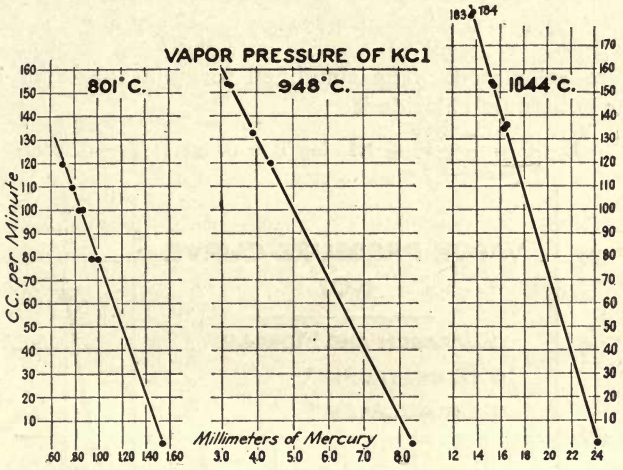


FIG. 4

The results of the experiments with potassium chloride at three temperatures are given in Table II. In Fig. 4 these results are plotted, using the partial pressures of potassium chloride as abscissas and the speed

TABLE II—VAPOR PRESSURE OF POTASSIUM CHLORIDE

Expt. No.	Cc. per Minute	Minutes	Nitrogen Millimoles	—KCl Grams	Volatilized— Millimoles	Partial Pressure Mm. Hg	°C.
46	78.2	23	80.3	0.0074	0.099	0.93	802
47	77.9	23	80.0	0.0078	0.105	0.99	801
50	100.1	18	80.5	0.0068	0.091	0.85	801
51	99.8	18	80.1	0.0065	0.087	0.82	803
53	108.8	16	77.7	0.0059	0.079	0.77	800
54	118.6	15	79.4	0.0054	0.072	0.69	800
55	118.7	15	79.5	0.0054	0.072	0.69	802
58	119.9	15	80.2	0.0337	0.452	4.24[1]	945
59	119.7	15	80.2	0.0338	0.453	4.25[1]	945
60	132.2	14	82.7	0.0318	0.426	3.88	948
61	132.9	13	77.1	0.0297	0.398	3.89	949
62	153.0	11	75.1	0.0244	0.327	3.28	948
63	153.5	11	75.4	0.0239	0.321	3.21	947
65	184.3	10	82.3	0.1146	1.54	13.9	1040
66	183.0	10	81.6	0.1110	1.49	13.6	1046
67	152.9	11	75.0	0.1162	1.56	15.5	1045
68	154.0	12	82.5	0.1268	1.70	15.3	1042
69	135.9	13	78.8	0.1313	1.76	16.6	1044
70	134.2	13	77.9	0.1285	1.72	16.4	1046

[1] In plotting the line to determine the vapor pressure, the values 4.36 and 4.37 corresponding to the temperature 948° were used.

of the gas stream in cubic centimeters per minute as ordinates. The values for the vapor pressures obtained by reading the partial pressures at zero speed are: 1.54 mm. at 801°, 8.33 mm. at 948°, and 24.1 mm. at 1044°.

To extend the usefulness of the data obtained, the vapor pressure curve for potassium chloride from 800° to 1500°, the boiling point determined by Borgstrom,[4] was constructed. Using the values for P found at 801° and 1044°, together with the boiling point, 1500°, the values of the constants in the empirical and approximate formula of Nernst[8]

$$\text{Log P} = \frac{\lambda_o}{4.571\,T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C$$

were calculated. The simplified formula thus found for potassium chloride is:

$$\text{Log P} = \frac{-5326}{T} + 1.75 \log T + 0.000511\,T - 0.7064$$

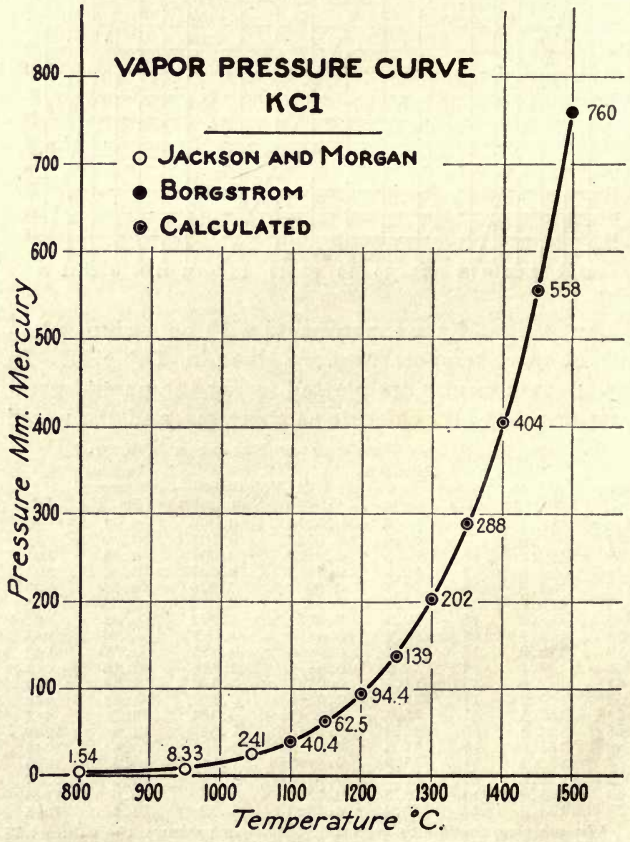


FIG. 5

TABLE III—VAPOR PRESSURES OF POTASSIUM CHLORIDE BETWEEN 800° AND 1500° C.

Temperature ° C.	Temperature ° Abs.	Pressure Calculated Mm. Hg	Pressure Observed Mm. Hg
801	1074	1.54	1.54
948	1221	9.06	8.33
1044	1319	24.1	24.1
1100	1373	40.4	..
1150	1423	62.5	..
1200	1473	94.4	..
1250	1523	139.0	..
1300	1573	202.0	..
1350	1623	288.0	..
1400	1673	404.0	..
1450	1723	558.0	..
1500	1773	760.0	760.0

The points on the vapor pressure curve calculated by this formula are given in Table III. The curve drawn through these points is shown in Fig. 5.

An approximate value for the latent heat of evaporation of potassium chloride can also be calculated from its vapor pressures by means of the van't Hoff equation written in the form:[9]

$$\text{Log}\frac{P_1}{RT_1} - \log\frac{P_2}{RT_2} = \frac{\lambda}{4.571}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The results of these calculations are given in Table IV.

TABLE IV—LATENT HEAT OF EVAPORATION OF POTASSIUM CHLORIDE CALCULATED FROM VAN'T HOFF'S EQUATION

Temperatures ° C.	Pressures Mm. Hg	Molecular Heat of Evaporation λ
801	1.54	
		—27,600
948	8.33	
		—32,800
1044	24.1	
		—32,000
1500	760.0	
MEAN VALUE.....		—30,800

VAPOR PRESSURE OF POTASSIUM CARBONATE

Potassium carbonate was the salt used in the first vapor pressure determinations made because it was thought that the conditions of volatilization of potash from potassium carbonate most nearly approach the condition of volatilization of potash from a cement mixture to which no special volatilizing or releasing reagent has been added. The salt used was a special grade of chemically pure potassium carbonate. When kept in a glass-stoppered bottle, which was nearly full and which was opened only as much as was necessary in removing the portions used, it did not seem to change in composition. The portions used for analysis or in the vapor pressure determinations were quickly transferred to a platinum boat and this at once placed in a glass-stoppered weighing bottle. The sample weighed in this manner gave on analysis by evaporating in platinum with an excess of sulfuric

acid, heating over a Méker burner, and weighing as potassium sulfate, the following results:

	Per cent	
	K_2O	K_2CO_3
(*a*)	65.17	95.61
(*b*)	65.31	95.83
(*c*)	65.19	95.65
(*d*)	65.21	95.69
MEAN	65.22	95.70

The results by the perchlorate method which would separate any sodium present were:

	Per cent	
	K_2O	K_2CO_3
(*e*)	65.22	95.70
(*f*)	65.15	95.59
MEAN	65.19	95.65

The sample, therefore, is practically free from sodium, and qualitative tests showed it to be free from appreciable amounts of other impurities, except moisture and possibly bicarbonate. On account of the absence of nonvolatile impurities the amount of potassium oxide remaining after a vapor pressure determination was found by dissolving the residue from the platinum boat in a platinum dish, evaporating with an excess of sulfuric acid, and weighing the potassium sulfate formed.

After numerous unsuccessful attempts to obtain constant weight and constant composition by drying the salt at temperatures from 120° to 900° C., it was decided to use the sample as analyzed above. Attention is therefore called to the fact that the sample used contained about 4 per cent of moisture, and to the probability of the results as reported being slightly higher than the true vapor pressures of anhydrous potassium carbonate, due to the formation of a small amount of potassium hydroxide in heating the undried salt.

To calculate the partial pressure of the vapor of the potassium salt it is necessary to make an assumption regarding the molecular weight in the vapor state. In these experiments the amount of carbon dioxide absorbed by soda lime in the absorbing train agrees roughly with the amount of potassium oxide lost by volatilization. It seems probable, therefore, that potassium carbonate on volatilizing decomposes as follows:

$$K_2CO_3 \longrightarrow K_2O + CO_2$$

Hence the vapor pressures were calculated for K_2O, using the assumed molecular weight of 94.2. In the calculations the number of millimoles of carbon dioxide was included in the total number of millimoles

whenever the amount of carbon dioxide evolved was sufficient to affect materially the final results.

The data and results of the experiments at two temperatures are given in Table V, and the plots of the results giving the vapor pressures at these temperatures are shown in Fig. 6. The vapor pressures thus obtained are: 1.68 mm. at 970° and 5.0 mm. at 1130° C.

TABLE V—VAPOR PRESSURE OF POTASSIUM OXIDE IN POTASSIUM CARBONATE

Expt. No.	Cc. per Min.	Minutes	Millimoles of N_2	Millimoles of CO_2	Millimoles of H_2O	K_2O Lost Grams	K_2O Lost Millimoles	Partial Pressure of K_2O Mm. Hg	°C.
4	78	23	79.4	0.1	1.0	0.0068	0.072	0.68	970
5	79	22	76.8	0.1	0.9	0.0083	0.088	0.86	970
6	51	37	83.6	0.1	1.5	0.0109	0.116	1.03	970
7	51	36	81.6	0.1	1.1	0.0103	0.109	1.01	970
10	35	50	77.3	0.1	1.0	0.0119	0.126	1.21	970
11	35	50	77.7	0.1	0.7	0.0122	0.130	1.25	970
15	51	35	78.4	0.5	0.9	0.0390	0.414	3.9	1130
16	51	35	78.4	0.5	1.1	0.0471	0.500	4.7	1130
17	80	23	80.0	0.4	1.1	0.0311	0.330	3.1	1130
18	80	22	77.7	0.4	1.0	0.0309	0.328	3.1	1130
19	102	16	71.8	0.4	1.1	0.0243	0.258	2.7	1130

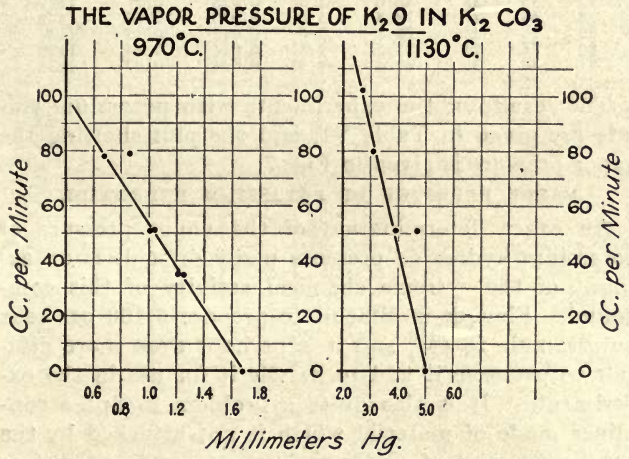


FIG. 6

VAPOR PRESSURE OF POTASSIUM SULFATE

On account of the impossibility of obtaining correct results in the determination of either the potassium or the sulfate radical in potassium sulfate by the ordinary methods of quantitative analysis, the salt used in these vapor pressure measurements was prepared by treating some of the same potassium chloride as was used in the vapor pressure determinations of that salt with pure sulfuric acid in a platinum dish, and heating the resulting potassium sulfate over a Méker burner to constant weight. Since this temperature was not high enough to melt the potassium sulfate, before

using it in a determination it was melted in a platinum boat by being placed for 2 or 3 min. in the vapor pressure tube. It was found that no loss of weight resulted. An examination of the residue after a series of vapor pressure determinations by evaporating it in platinum with an excess of sulfuric acid and heating to constant weight showed that the residue also was pure potassium sulfate. Hence as there was no evidence of dissociation on heating and since the vapor density of potassium sulfate has never been determined, the assumption was made that the vapor corresponds to the formula K_2SO_4, molecular weight 174.4. The partial pressures of potassium sulfate were calculated on the basis of this assumption.

TABLE VI—VAPOR PRESSURE OF POTASSIUM SULFATE

Expt. No	Cc. per Min.	Minutes	Millimoles N_2	K_2SO_4 Lost— Milligrams	Millimoles	Partial Pressure Mm. Hg	°C.
75	37	48	79.4	5.2	0.030	0.29	1129
76	37	48	79.6	6.7	0.038	0.36	1129
77	46	38	78.0	4.9	0.028	0.27	1127
78	65	27	78.5	3.5	0.020	0.19	1129
79	76	23	78.1	2.6	0.015	0.15	1127
80	76	23	77.5	2.5	0.014	0.14	1126
81	49	38	82.6	4.1	0.024	0.22	1131

The results of the experiments with potassium sulfate are given in Table VI, and the plot showing the vapor pressure is given in Fig. 7.

VAPOR PRESSURE OF POTASSIUM HYDROXIDE

An exact determination of the vapor pressure of potassium hydroxide presents many difficulties on account of the extreme chemical activity of this compound. First, it is difficult to prepare a 100 per cent pure sample to use, and it is perhaps even more difficult to preserve it and to handle it for use in the experiments. It is also quite a problem to find a container made of material which is not attacked by the hot liquid, and of such shape that it will allow free evaporation and at the same time prevent loss of the liquid, which shows an unusual tendency to creep out of the container. Again there is undoubtedly some action between the vapors and the walls of the tube and ends of the plugs in the apparatus, and finally the composition and molecular weight of the vapor is not known. In view of the other uncertainties it did not seem to be worth while to spend a large amount of time preparing a special grade of pure hydroxide for the determinations, and it was thought that results which would give much light on the question of the commercial volatilization of potash could be obtained by use of a sample of chemically pure potassium hy-

droxide from a reliable dealer in chemicals. The material used, therefore, was from a newly opened bottle of chemically pure potassium hydroxide, purified by alcohol and cast into sticks. A stick of this material was rapidly crushed in a mortar into pieces weighing from 0.3 to 0.6 g., and these pieces were quickly placed in separate glass-stoppered weighing bottles and weighed as soon as possible. Some of the weighed pieces were used in the vapor pressure determinations and others were analyzed. The analyses by the perchloric acid method gave for the total potassium calculated as hydroxide: 84.67, 84.35, 84.80, 84.45, and

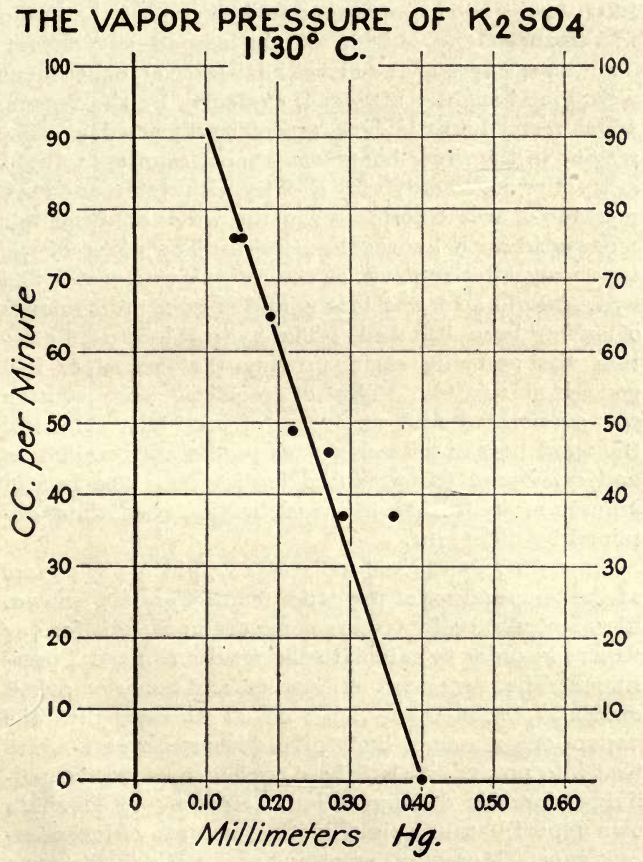


FIG. 7

83.98, an average of 84.45 per cent for all of the determinations made. The main impurities, water and carbonic acid, should not materially interfere with the volatilization.

In solving the question of containers, both platinum and nickel were tried before silver was finally selected. In the final experiments a weighed piece of potassium hydroxide was contained in a boat of pure silver foil. This inner silver boat was placed in an outer boat also of silver foil, and slightly longer, wider, and shallower. The outer boat in turn was set into a larger nickel boat which served as a support in placing the charge in and removing it from the vapor pressure tube. The object of the outer silver boat was to catch the liquid potassium hydroxide which creeps over the sides of the inner silver boat and thus prevent its loss or its action on the nickel boat. This it did successfully, for in no case was there evidence that the liquid had reached the outside of the second silver boat. The upper edges of the nickel boat after an experiment were found slightly attacked, evidently by the vapors, which formed a little dark, greenish gray powder. The residue in the silver boats was almost colorless to light gray, effervesced only very slightly with water, and gave no odor of free chlorine when the water solution was made acid with hydrochloric acid. The silver of the two boats after removal of the residue with water and hydrochloric acid was bright and showed no evidence of having been attacked. The hydrochloric acid solution was perfectly clear, proving that no silver had gone into solution. This hydrochloric acid solution was evaporated with an excess of perchloric acid, and the total potassium weighed as potassium perchlorate and calculated to potassium hydroxide. The loss of potassium hydroxide by volatilization was then obtained by difference.

Since the formula and molecular weight of the vapors at the temperature of the experiments were not known, it was necessary to assume a molecular weight for the vapors in order to calculate the results as partial pressures. The statement of Roscoe and Schorlemmer,[10] evidently based upon the work of Deville, that the vapors of potassium hydroxide decompose at a white heat into potassium, hydrogen, and oxygen, needs qualifying, for this decomposition, according to Deville's own report,[11] takes place in the presence of incandescent iron. Moreover, according to Deville in the same report, the decomposition ceases if the temperature is lowered below a white heat. Further, according to Watts,[12] who does not give the authority for the statement, potassium hydroxide when heated alone does not decompose at any temperature. Since the tempera-

ture of the experiments here reported, 795° C., is far below a white heat, it is not probable that dissociation takes place to an appreciable extent. Hence it was most simple and seemed entirely justifiable to assume that the vapors given off were KOH with a molecular weight of 56.1.

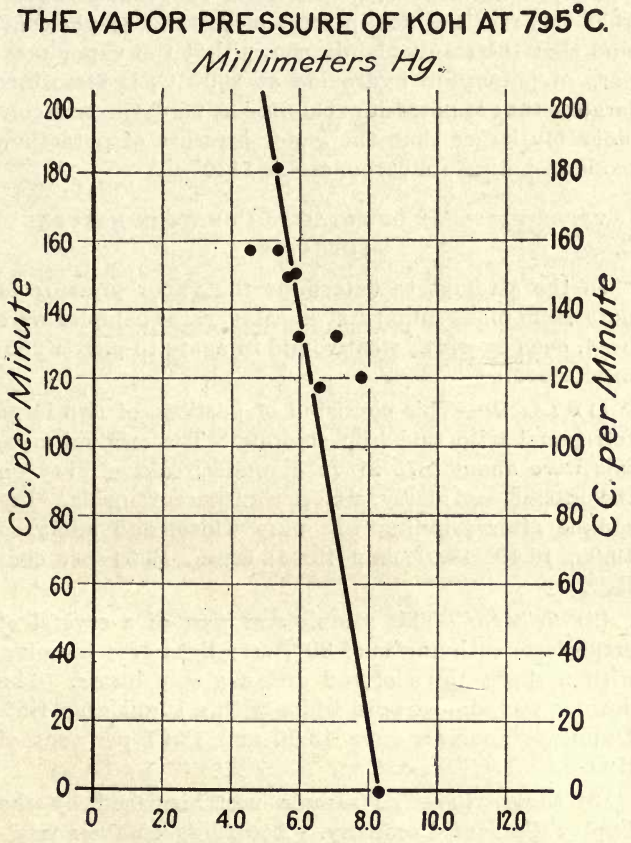


FIG. 8

The data of the experiments, together with the results calculated on this basis, are given in Table VII,

TABLE VII—VAPOR PRESSURE OF POTASSIUM HYDROXIDE

Expt. No.	Cc. per Min.	Minutes	Millimoles N_2	KOH Volatilized Milligrams	KOH Volatilized Millimoles	Partial Pressure Mm. Hg	° C.
127	182	10	81.2	32.5	0.58	5.4	794
129	158	11	77.9	27.2	0.48	4.6	795
180	158	11	77.8	31.4	0.56	5.4	790
181	151	12	80.8	35.3	0.63	5.9	793
182	150	12	80.4	34.4	0.61	5.7	795
183	133	13	77.4	34.7	0.62	6.0	794
184	133	13	77.2	41.3	0.73	7.1	795
185	121	15	81.2	44.0	0.78	7.2	794
186	118	15	78.7	38.5	0.69	6.6	795

and these results are plotted and extrapolated in Fig. 8. On account of the possibility of variation in the

composition of the pieces of the sample used in the different experiments, which variation probably explains the fact that three of the nine points are at slight variance with the mean straight line, a high degree of accuracy is not claimed for the vapor pressure found, namely, 8 mm. at 795° C. It is believed, however, that this result is not in error more than 25 per cent, and that the result plainly shows that the vapor pressure of potassium hydroxide at 800° C. is almost as large as that of potassium chloride at 950° C., and considerably larger than the vapor pressure of potassium oxide in potassium carbonate at 1130° C.

VAPOR PRESSURE OF POTASSIUM OXIDE IN NATURAL SILICATES

In the attempt to determine the vapor pressure of potassium oxide in natural silicates, three samples were used, each of which was ground in agate to pass a 200-mesh sieve.

(1) *Leucite*—This consisted of portions of two large tetragonal trisoctahedron crystals. The original crystals were about 0.75 in. in diameter, colored gray on the outside, and glassy, almost transparent, inside. The sample after grinding was pure white, and analyzed 19.05, 19.10, 18.97, and 19.04; mean, 19.04 per cent K_2O.

(2) *Feldspar*—This sample was part of a crystal of orthoclase, with angles of 90°, very light gray in color, with a slight tinge of red and a glassy luster. The powder was almost pure white with a slight gray tint. Duplicate analyses gave 13.90 and 13.97 per cent of K_2O.

(3) *Glauconite*—The sample was furnished by the Coplay Cement Company. According to their analysis it contained:

	Per cent
Silica	40.56
Alumina and ferric oxide	30.40
Calcium oxide	9.58
Magnesium oxide	2.09
Potassium oxide	6.06
Loss on ignition	10.52

It was found to contain iron equivalent to 20.85 per cent of ferric oxide, and analysis gave 6.10, 6.04, 6.07, 6.03, and 6.00; mean, 6.05 per cent of K_2O.

In the experiments a weighed portion of about 0.5 g. was heated for 48 min. in a platinum boat in the vapor pressure tube, while dry nitrogen was passed through at a speed of 35 to 37 cc. per minute. Within

the limit of accuracy of the analyses (about 0.0005 g. of K_2O in a 0.5 g. sample) there was no loss of potassium in any of the silicates at 1335° C. or lower. Hence the vapor pressure of potassium oxide in these three natural silicates when heated alone at temperatures under 1350° C. is entirely negligible.

The results of experiments with the three silicates, showing loss of weight and change of state at three temperatures, are given in Table VIII.

TABLE VIII—RESULTS OF HEATING POTASSIUM-BEARING SILICATES FOR 48 TO 50 MIN.

Expt. No.	Temp. ° C.	Silicate Used	Loss of Weight Per cent	Loss of K_2O	Residue, Appearance, etc.
25	1130	Leucite	0.60	None	White, no sintering
28	1245	Leucite	0.73	None	White, trace of sintering
32	1335	Leucite	0.74	None	White, slightly sintered
24	1130	Feldspar	0.00	None	Pale gray, no sintering
27	1245	Feldspar	0.04	None	Pale gray, slightly sintered
31	1335	Feldspar	0.08	None	Nearly all fused to a colorless glass
23	1130	Glauconite	11.59	None	Reddish brown, sintered
29	1245	Glauconite	12.13	None	Dark red, fused
30	1335	Glauconite	12.47	None	Dark greenish glass

SUMMARY

I—The vapor pressure method of von Wartenberg has been adapted to the study of the vapor pressures of potassium compounds and the vapor pressures shown in the following table have been determined.

VAPOR PRESSURES OF POTASSIUM COMPOUNDS EXPRESSED IN MILLIMETERS OF MERCURY

Temp. ° C.	Hydroxide	Chloride	Oxide in Carbonate	Sulfate	Natural Silicates
795	8	...	..	...	..
801	..	1.54	..	...	..
948	..	8.33	..	...	..
970	..	...	1.68	...	..
1044	..	24.1	..	...	..
1130	..	...	5.0	0.4	0
1335	..	...	..	...	0

II—From the results of the vapor pressure measurements with potassium chloride at 801° and 1044° C., together with the boiling point of this compound as given by Borgstrom, the Nernst vapor pressure formula for potassium chloride has been calculated to be:

$$\text{Log } P = \frac{-5326}{T} + 1.75 \log T + 0.000511\,T - 0.7064$$

By means of this formula the vapor pressure curve for potassium chloride from 800° to 1500° C. has been constructed.

III—It has been established by these vapor pressure measurements that the order of volatility of those potassium compounds which are most important in the recovery of potash from cement or other silicate mixtures is as follows: Hydroxide, chloride, oxide from carbonate, sulfate, and natural silicates.

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New Method for the Determination of Potassium in Silicates

The usual methods of determining potassium in silicates, particularly in fused residues, have been found to present numerous difficulties. In the work[1] on the volatilization of potassium oxide from natural silicates, a combination of the J. Lawrence Smith method and the perchloric acid method was used in determining the amount of potassium in the residues from an experiment, whenever that residue was in such form that it could be removed from the platinum boat in which the experiment was made, and ground to a powder. In many cases the residue had fused, and to remove it from the boat it was necessary to dissolve it with hydrofluoric acid. In such cases a combination of the hydrofluoric acid method of Krishnayya[2] and the perchloric acid method was employed. While it was possible by either of these methods to obtain results in duplicate that agreed fairly well, the results by one method did not agree with those by the other, and both methods were tedious and time-consuming. It was therefore evident that if much work was to be done on the volatilization of potassium salts from silicate mixtures, it would be necessary to find a more rapid and more reliable method for the determination of potassium in silicates.

In order that the method might be applicable to residues which had been melted and solidified in a platinum boat, it was necessary to decompose the silicate with hydrofluoric acid, and hence it was decided to get rid of the fluorine by evaporating with perchloric acid instead of with sulfuric acid. This was found to work very satisfactorily. Only in mixtures containing considerable calcium is it necessary to repeat the evaporation after taking up with hot water and adding more perchloric acid to transform the fluorides completely to perchlorates. This procedure offers

[1] Pages 24-25.

[2] *Chem. News*, **107** (1913), 100.

an additional advantage, since the perchlorates of all of the bases, except potassium, commonly found in silicates, are soluble in the alcohol wash used in the regular perchlorate method.[1] Hence the residue after evaporation can be treated at once with alcohol wash, and the insoluble potassium perchlorate transferred from the dish in which the silicate is dissolved directly to the Gooch crucible in which it is weighed. The only common substances likely to interfere in the analysis are ammonium and sulfur compounds. The ammonium compounds can be removed by preliminary heating, and some experiments, which will be mentioned later, seem to show that any interference of the sulfur compounds can be estimated and a correction applied. The method has been used on a large number of mixtures of feldspar and glauconite with sodium chloride, calcium chloride, calcium carbonate, and limestone, and there was no interference from sulfur compounds. This was demonstrated by the facts that the water solution of the weighed perchlorate precipitate was found in every case to be free from soluble sulfates, and that the weight of the Gooch crucible after each determination showed the absence of insoluble sulfates.

In the method finally used, after the silicate was decomposed the excess of hydrofluoric acid was expelled by evaporating at a low heat on a sand bath, and the residue was dissolved by warming with 3 *N* hydrochloric acid. This gave an opportunity to see that the decomposition of the silicate had been complete, and admitted of the removal of the platinum boat.

DETAILS OF METHOD

From 0.3 to 0.6 g. of the silicate is decomposed by digesting at room temperature with an excess of hydrofluoric acid, and this excess is removed by evaporating to dryness at low temperature on a sand bath. About 25 cc. of 3 *N* hydrochloric acid are added, and the mixture warmed until all except a small amount of calcium fluoride is dissolved. An excess, about 10 cc., of 10 per cent perchloric acid is added, and evaporation continued on a sand bath until dense white fumes of perchloric acid are obtained. At this point the residue may be allowed to go to dryness over night on an electrically heated sand bath designed for this purpose and regulated so that the heat is not high enough to decompose the perchlorates in the residue.

[1] Scholl, *J. Am. Chem. Soc.*, **36** (1914), 2085.

The residue is then taken up with hot water, in which all except a small amount of calcium fluoride should be soluble, 1 or 2 cc. of 10 per cent perchloric acid are added, and the evaporation to dense white fumes repeated. If the residue from the first evaporation is not completely soluble in hot water plus perchloric acid, the residue from the second evaporation is dissolved in hot water, a little more perchloric acid is added, and the liquid again evaporated to white fumes. The evaporation in every case is repeated once after the residue is completely soluble in hot water. Usually it is necessary to evaporate only twice.

The residue from the final evaporation is allowed to cool thoroughly. It is then treated with about 20 cc. of alcohol wash (97 to 98 per cent alcohol containing 1 cc. of 60 per cent perchloric acid per 300 cc.) and allowed to digest with frequent stirring for at least 15 min. The alcohol solution must be cold when filtered. The solution is finally decanted through asbestos in a Gooch crucible, and the potassium perchlorate washed by decantation and also in the crucible with small portions of the alcohol wash. The precipitate is particularly satisfactory to work with, showing no tendency to creep or stick to the platinum dish, and the washing can be made complete with a total volume of filtrate and washings of 50 to 75 cc. The precipitate is dried at least 30 min. at about 130° C. Its composition is $KClO_4$, the factors of which are 0.340 for K_2O and 0.538 for KCl. The weighed salt is dissolved from the asbestos felt with hot water, and the crucible, after drying, is then ready for the next determination.

INTERFERENCE OF SULFUR COMPOUNDS

The materials analyzed by the above method were free from sulfur compounds in amounts sufficient to interfere with the method, as was shown by the absence of sulfates in the weighed potassium perchlorate. A few experiments were made, however, to show what might be the interference of sulfur, and the suggestions from these experiments are of interest. The weight of potassium perchlorate obtained from equal volumes of a potassium chloride solution, both with and without addition of 2 cc. of 0.1 *N* sulfuric acid, showed in the presence of an excess of perchloric acid no potassium sulfate was formed, and a test of the solution of the weighed perchlorate in water proved that it contained no sulfate.

If sulfur is present in the silicate analyzed it will either be volatilized during the evaporations with hydrofluoric and perchloric acids or else will remain in the final residue as a sulfate. To interfere with the determination of potassium as perchlorate, the sulfate radical must be combined with a base whose sulfate is insoluble in alcohol containing perchloric acid. Of the bases usually present in silicates, especially the silicates used in cement making, the sulfates of ferric iron, aluminium, manganese, and magnesium are soluble in alcohol. On the other hand, those of barium and strontium are so insoluble in water that they will be left on the asbestos felt when the residue is dissolved in hot water, and can be corrected for in weight. Since potassium sulfate is not formed in the presence of an excess of perchloric acid, this leaves only calcium sulfate and sodium sulfate, which are insoluble in alcohol but soluble in water, and hence may be weighed as potassium perchlorate in the method given.

SULFATES IN THE POTASSIUM PERCHLORATE PRECIPITATE

Expt. No.	KCl Solution Taken. Cc.	H_2SO_4 0.1 *N* Added. Cc.	$CaCl_2$ *N* Added Cc.	Ppt. Found. Gram $KClO_4$	Found Gram $BaSO_4$	$2CaSO_4 + H_2O$ Equivalent to $BaSO_4$	Corrected $KClO_4$	Calculated KCl
a	10	..	..	0.1849	..	..	0.1849	0.0995
b	10	..	..	0.1854	..	..	0.1854	0.0998
c	10	2	..	0.1856	..	..	0.1856	0.0999
d	10	2	..	0.1859	..	..	0.1859	0.1000
e[1]	10	2	2	0.2003	0.0236	0.0147	0.1856	0.0999
f[1]	10	2	2	0.2006	0.0239	0.0149	0.1857	0.0999

[1] Experiments *e* and *f* show definitely that even in the presence of both calcium and sulfate radicals very accurate results can be obtained by this method.

Two experiments with the potassium chloride solution mentioned above, to which both sulfuric acid and calcium chloride were added before it was evaporated with perchloric acid, showed that all of the sulfate radical added was present as a calcium salt in the perchlorate precipitate. The residue, after weighing, was dissolved in water, hydrochloric acid was added, and the sulfate determined as barium sulfate. If the amount of calcium sulfate, $2CaSO_4.H_2O$, equivalent to the barium sulfate found, is deducted from the weight of the perchlorate precipitate, the amount of potassium perchlorate in this case agrees remarkably well with the amount found for the same volume of potassium chloride solution in the other experiments. The tabulation of these results is given in the accompanying table. No experiments have yet been made on the

interference of sulfates in the presence of other bases, but it is believed that with the bases usually found in cement materials, where there is a great excess of calcium, any sulfate in the perchlorate precipitate will be present as $2CaSO_4.H_2O$, or if not all combined with calcium, the rest will be combined as anhydrous sodium sulfate whose molecular weight, 142, is so close to the weight of $CaSO_4 + {}^1/_2H_2O$, 145, that no serious error is introduced by correcting for a small amount of sulfate in the way indicated.

SUMMARY

It is believed that for the determination of potassium alone in silicate materials which are free from appreciable amounts of sulfur compounds the method here given is the simplest and most accurate yet devised. It has the following advantages:

1—It is not necessary to have the material finely ground.

2—There is no chance for loss of potassium by volatilization, as is the case in other methods where the salts, usually chlorides, are heated to decompose the silicate or to remove ammonium compounds.

3—All separations of other elements by precipitation which might cause loss of potassium salts by adsorption, formation of double salts, etc., are avoided.

4—The only time-consuming operations are the evaporations, which may be carried on with very little attention, especially on an electrically heated sand bath, as there is absolutely no tendency to spatter when a moderate heat is used.

5—The potassium compound which is filtered and weighed is, under the conditions of the method, the most insoluble of any used in the determination of potassium, and is absolutely constant in composition.

An Application of the Vapor Pressures of Potassium Compounds to the Study of the Recovery of Potash by Volatilization

The immense amount of work which has been done upon the extraction of potash from complex mineral silicates is clearly shown by a bibliography on the subject published at the beginning of 1918 by E. C. Buck.[1] This bibliography refers to no less than one hundred and thirty patents and fifty general articles published in the six years, 1912 to 1917. Of the proposed processes for the recovery of potassium in the form of soluble salts from the natural potassium-bearing silicates fully one-third are based upon the separation of the potassium compounds by volatilization. In spite of this great amount of work and with the stimulus of the inflated prices of potassium compounds, only a very few of the numerous processes proposed have been put into actual operation on a commercial scale. It was decided, therefore, to apply the knowledge obtained from the vapor pressure experiments recorded in a previous paper[2] to an investigation of the volatilization of potassium compounds from mixtures of silicates with releasing and volatilizing agents. It was thought that this investigation would show the reason for the apparent failure of so many of the proposed methods and might suggest the conditions for a method which would be commercially successful. In the light of the vapor pressure determinations the methods involving the use of a chloride seemed to be most practicable, and glauconite, or greensand, was thought to be the most promising of the natural silicates containing potassium. Hence the first experiments were made with mixtures of greensand and calcium chloride.

[1] *Met. Chem. Eng.*, **18** (1918), 33, 90.

[2] Pages 5-25.

VOLATILIZATION OF POTASH FROM MIXTURES OF GREENSAND AND CALCIUM CHLORIDE

In these experiments a carefully weighed amount of greensand, powdered to pass a 200-mesh sieve, was well mixed in a small platinum boat with approximately 10 per cent of its weight of powdered, anhydrous, C. P. calcium chloride. The boat and contents were heated in the vapor pressure apparatus in a current of nitrogen dried with calcium chloride, as has been described under the determination of the vapor pressure of potassium chloride.

Irregular results obtained at 1200° C. were thought to be due to the temperature being too low for complete fusion and rapid intermingling of the reacting substances. At 1300° the results of duplicate determinations agreed better, and the amount of potassium chloride volatilized varied with changes in the speed of the gas stream in such manner that it was possible to plot the partial pressures and obtain the vapor pressure of potassium chloride in the mixture. The value of 1.6 mm. of mercury thus obtained at 1300° bore, however, no apparent relation to the known vapor pressure of potassium chloride or to the amount of potassium in the mixture. The percentage of K_2O volatilized at 1300° was found to be only slightly greater than at 1200°. On account of the claim of Spackman and Cornwell[1] that the presence of water vapor in a cement kiln aids in the formation

TABLE I—VOLATILIZATION OF POTASH FROM MIXTURES OF GREENSAND AND CALCIUM CHLORIDE

Expt. No.	Minutes	Temperature ° C.	Weight of Charge Greensand	Weight of Charge $CaCl_2$	K_2O in Charge	K_2O in Residue	Per cent K_2O Volatilized
82	12	1204	0.5993	0.060	0.0363	0.0320	12
83	12	1203	0.6744	0.075	0.0408	0.0354	13
84	14	1208	0.6153	0.061	0.0373	0.0332	11
85	14	1205	0.5710	0.064	0.0346	0.0301	13
86	16	1201	0.7117	0.072	0.0431	0.0385	11
87	15.5	1202	0.6660	0.066	0.0403	0.0350	13
88	18	1303	0.6364	0.065	0.0386	0.0319	17
89	11	1301	0.6008	0.061	0.0364	0.0310	15
90	11	1300	0.6086	0.061	0.0369	0.0313	15
91	18	1301	0.6314	0.065	0.0383	0.0317	17
92	26	1302	0.5819	0.058	0.0353	0.0286	19
93	26	1302	0.5879	0.059	0.0356	0.0284	20
94[1]	26	1297	0.5541	0.055	0.0336	0.0281	16
95[1]	26	1303	0.5728	0.057	0.0347	0.0277	20
96[1]	16	1298	0.6059	0.061	0.0367	0.0311	15
97[1]	17	1302	0.5900	0.059	0.0358	0.0306	14
98[1]	12	1299	0.6235	0.062	0.0377	0.0310	18
99[1]	12	1301	0.6338	0.063	0.0384	0.0333	13

[1] The gas used was a mixture of nitrogen and dry steam.

of soluble potassium compounds from potassium-bearing silicates and acid-forming gases. *e. g.*, chlorine from the decomposition of chlorides added

[1] U. S. Patent 1,202,327 (1916); *C. A.*, **11** (1917), 89.

with the charge, experiments were made in which water vapor was mixed with the nitrogen used in the vapor pressure tube. The results of these experiments show plainly that no advantage in the formation and volatilization of potassium chloride is gained by the use of water vapor with a mixture of calcium chloride and greensand.

The figures obtained with mixtures of greensand and calcium chloride are given in Table I.

VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATES WITH LIME

The next experiments were with calcium oxide as a releasing agent. On account of the number of experiments necessary to obtain results which can be plotted and extrapolated to vapor pressures, and on account of the difficulty in finding any definite rela-

TABLE II—MIXTURES OF SILICATES AND LIME USED IN VOLATILIZATION EXPERIMENTS

Mixture No.	Materials Used	Proportions Grams	Per cent of CaO after Heating Calculated	Per cent of K_2O in Raw Mixture
I	Greensand	10		
	$CaCO_3$ pptd.	22	64	1.90
3	Greensand	30		
	Limestone	70	50	2.38
VI	Greensand	10		
	Calcium hydroxide	15	62	2.46
VIII	Greensand	6		
	$CaCO_3$ pptd.	9	48	2.42
VII	Greensand	6		
	$CaCO_3$ pptd.	6	38	3.03
III	Feldspar	3		
	$CaCO_3$ pptd.	9	65	3.50
V	Feldspar	3		
	$Ca(OH)_2$	6	64	4.70

TABLE III—VOLATILIZATION OF POTASH FROM SILICATE AND LIME MIXTURES (Heated 11 min. at 1300° C.)

Expt. No.	Mixture No.	Cc. N_2 per Min.	Water Vapor Mg.	Charge Grams	Loss in Weight Per cent	Mg. K_2O in Charge	Mg. K_2O in Residue	Per cent K_2O Volatilized
100	I	150	....	0.5754	34.9	10.9	2.7	75
101	I	117	....	0.5727	34.9	10.9	2.7	75
102	I	79	....	0.5529	35.0	10.5	2.4	77
106	I	150	10.9	0.5502	35.2	10.5	1.0	91
107	I	117	7.8	0.5695	35.2	10.8	1.1	90
108	I	80	6.0	0.5839	35.2	11.1	1.2	89
150	3	162	....	0.5588	32.9	13.3	9.3	30
151	3	134	....	0.5390	33.0	12.8	9.8	23
152	3	163	8.2	0.5242	33.5	12.5	6.1	51
153	3	132	7.2	0.5062	33.6	12.1	5.5	55
116	VI	161	....	0.5032	19.9	12.4	7.4	40
117	VI	135	....	0.4971	20.0	12.2	6.6	46
122	VI	161	13.7	0.5362	20.3	13.2	5.8	55
148	VIII	160	....	0.4763	30.6	11.6	10.4	10
146	VIII	160	19.9	0.4732	30.7	11.4	10.0	12
142	VII	160	....	0.4140	27.3	12.5	11.5	8
144	VII	160	5.8	0.4290	27.1	13.0	12.1	7
112	III	162	....	0.3100	34.0	10.9	9.9	9
113	III	134	....	0.3077	34.0	10.8	9.7	10
118	III	158	7.6	0.3030	34.3	10.6	8.5	20
119	III	133	6.6	0.3050	34.3	10.7	8.4	22
114	V	164	....	0.3030	17.7	14.5	13.5	7
115	V	133	....	0.2992	17.8	14.3	13.1	8
120	V	160	12.3	0.3262	18.1	15.7	13.5	14
121	V	146	11.1	0.3116	18.3	15.0	12.8	15

tion between the vapor pressures of potassium compounds in the mixtures and the vapor pressures of the pure compounds involved, it was decided to run the experiments in duplicate. The speed of the gas stream was varied, but the time of the experiment was kept constant. The results were expressed in terms of the percentage of potassium oxide volatilized. The knowledge of the vapor pressure of the pure potassium compounds involved was then used in interpreting the results. In the experiments with lime as a releasing agent the mixtures given in Table II were used. The results of heating these mixtures for 11 min. at 1300° C. are shown in Table III.

A consideration of the results of the experiments given in Table III leads to the following conclusions:

(1) The low volatilization in the feldspar mixture (III) is due to the fact that the vapor pressure of potassium oxide alone is too low at 1300° C. to cause rapid and complete volatilization of the potassium in the mixture. The vapor pressure of potassium oxide from potassium carbonate has been found to be 1.68 mm. at 970° C. and 5.0 mm. at 1130°, while the vapor pressure of potassium chloride at these temperatures is 10.1 mm. and 52.7 mm., respectively. If the vapor pressure curve for potassium oxide in potassium carbonate has the same general form as that for the chloride, the vapor pressure of the oxide at 1300° C. would be about 13 mm. It would seem that the vapor pressure of potassium oxide in the highly limed mixture of silicate and lime is not greater than that of potassium oxide in the carbonate, and has probably about the same value as the vapor pressure of water at 15° C.

(2) The explanation of the higher results in the greensand mixture (I) lies in the fact that greensand is a hydrated silicate. Accordingly, any K_2O formed by the action of CaO upon the greensand is formed in the presence of water vapor which is being evolved from the silicate. This affords an excellent opportunity for the formation of potassium hydroxide, provided the reaction

$$K_2O + H_2O \longrightarrow 2KOH$$

is not completely reversed at 1300° C. The statements of Deville,[1] quoted by Roscoe and Schorlemmer,[2] and of Watts[3] are contradictory on this point, but it is believed that at a temperature of 1300°, or lower, the reaction of K_2O and H_2O to form potassium hydroxide must certainly take place at a speed which is not inappreciable. Now the vapor pressure of potassium hydroxide at 800° C. has been determined and found to be about as great as that of the chloride at 950° and considerably greater than that of the oxide from the carbonate at 1130°. At

[1] *Compt. rend.*, **45** (1857), 857.

[2] Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. II, "The Metals," **1907**, 321.

[3] Watts, "Dictionary of Chemistry," Vol. IV, **1868**, 702.

1300° the vapor pressure of potassium chloride is 202 mm., and at this temperature the hydroxide must be near its boiling point. Hence it is believed that when the greensand molecule reacts with calcium oxide at the high temperature of these experiments, a considerable portion of the potassium in the greensand forms potassium hydroxide with the oxygen and hydrogen which are combined in the silicate, and is thus volatilized from the mixture. In an attempt to aid the volatilization of potassium from the greensand and feldspar before the theory of the volatilization as given above had been fully developed, some experiments were made in which calcium hydroxide was substituted for calcium carbonate in the mixtures (V and VI). The use of calcium hydroxide did not aid the volatilization and it is not to be expected that it would, for this compound is dissociated into calcium oxide and water vapor so rapidly at the high temperature of the experiments and the water vapor is so quickly carried away from the mixture by the rapid stream of dry nitrogen used that there is little chance for the formation of potassium hydroxide. On the other hand, the water vapor from greensand is given off rather slowly, and since the hydrogen and oxygen exist closely associated with the potassium in the greensand molecule there is every chance for the formation and volatilization of potassium hydroxide.

(3) The results of the experiments in which nitrogen carrying a considerable amount of water vapor was used instead of dry nitrogen confirm in a very striking manner this new theory of the volatilization of potassium from mixtures of silicates with lime in about the proportions used in the manufacture of portland cement. According to the theory, the low volatilization of potassium from the feldspar and lime mixtures is due to the low vapor pressure of potassium oxide formed by interaction of the potassium aluminium silicate and calcium oxide, and the higher volatilization of the potassium from the greensand and lime mixtures is on account of the high vapor pressure of potassium hydroxide, which is formed along with potassium oxide by the action of calcium oxide on the *hydrated* potassium iron silicate. The potassium hydroxide thus formed may be dissociated at this high temperature, possibly according to the reaction:

$$2KOH \rightleftharpoons K_2O + H_2O$$

Hence it would be expected that a continuous and fairly large supply of water vapor in the atmosphere of the reaction chamber would prevent to some extent the dissociation of the potassium hydroxide and aid in the volatilization of potassium from the mixture. It would also be expected that the water vapor thus supplied would react to form hydroxide with the potassium oxide in the feldspar mixtures and increase the volatilization of potassium from these mixtures as well. The results of the experiments in which water vapor was used completely fulfilled these expectations, and thus confirmed the theory of the volatilization of potassium as developed above.

(4) The percentage of potassium volatilized from the mixture (3) of greensand with limestone is lower than that obtained

when either precipitated calcium carbonate or calcium hydroxide was used. This is probably due partly to the lower lime content of the mixture and partly to impurities present in the limestone. Even in this mixture, however, the volatilization was doubled by the use of water vapor.

(5) The very low volatilization of potassium in the greensand mixtures (VII and VIII) is due partially to the small percentage of lime in the mixtures, but mainly to the fact that these low lime mixtures at this temperature fuse completely, forming a glass in which the potassium is probably combined with the silica and thus dissolved in the other liquid silicates so that it is prevented from volatilizing both by being chemically combined in a rather nonvolatile compound and by being dissolved in a viscous liquid. Undoubtedly the small amount which was volatilized came off during the melting of the mixture. Naturally when potassium is held in a glassy silicate, water vapor cannot aid in its volatilization.

VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATES WITH LIME AND CALCIUM CHLORIDE

From our knowledge of the vapor pressures of the compounds involved it might be predicted that better results would be obtained in the volatilization of potassium from silicate mixtures containing both lime and calcium chloride, than from mixtures of silicates with either of these compounds alone.

In the experiments to test the efficiency of calcium chloride as a volatilizing agent when used in conjunction with lime as a releasing agent, the mixtures given in Table IV were used. Both were made in proportions which would give, after heating, a residue that approached portland cement in composition.

TABLE IV—MIXTURES OF SILICATES WITH CALCIUM CARBONATE AND CALCIUM CHLORIDE

Mixture No.	Materials Used	Proportions Grams	Per cent of CaO after Heating Calculated	Per cent of K_2O in Raw Mixture
II	Greensand	10		
	$CaCO_3$ pptd.	21		
	$CaCl_2$ anhyd.	1	65	1.90
IV	Feldspar	10		
	$CaCO_3$ pptd.	26		
	$CaCl_2$ anhyd.	2	65	3.70

The results of heating these mixtures for 11 min. at 1215° and at 1300° C. are given in Table V. The experiments with the greensand mixture at 1300° were made first. Since the volatilization was practically complete at this temperature, the experiments at 1215° were performed so as to find whether the use of water vapor had any influence on the volatilization of potash from cement mixtures when used in connection with a chloride.

TABLE V—VOLATILIZATION OF POTASH FROM MIXTURES OF SILICATE WITH LIME AND CALCIUM CHLORIDE
(Heated 11 Min. with 125 to 170 Cc. of Nitrogen Passing per Min.)

Expt. No.	Mixture No.	Temperature ° C.	Water Vapor Mg.	Charge Grams	Loss in Weight Per cent	—Mg. K_2O— in Charge	in Residue	Per cent K_2O Volatilized
103	II	1300	....	0.5603	36.0	10.7	0.3	97
104	II	1300	....	0.5618	35.9	10.7	0.3	97
105	II	1300	....	0.5629	36.1	10.7	0.2	98
109	II	1300	10.9	0.5132	36.2	9.8	0.3	97
110	II	1300	12.0	0.5551	36.2	10.5	0.3	97
111	II	1300	8.1	0.5350	36.2	10.2	0.2	98
132	II	1215	....	0.5223	36.2	9.9	0.7	92
133	II	1215	....	0.5301	36.2	10.1	Trace	..
134	II	1215	7.4	0.5301	36.2	10.1	0.8	92
135	II	1215	15.6	0.5257	36.2	10.0	0.4	96
136	IV	1215	....	0.3249	36.8	12.0	3.5	71
137	IV	1215	....	0.3056	36.9	11.3	3.1	73
138	IV	1215	13.7	0.3021	36.9	11.2	2.9	74
139	IV	1215	7.3	0.3149	36.9	11.6	3.0	74

The results of the experiments on mixtures of greensand and of feldspar with both calcium oxide and calcium chloride in proportions to give a residue which has about the composition of portland cement show that:

(1) The removal of potassium by volatilization from the greensand mixture is practically complete in 11 min. at a temperature as low as 1215° C., but the volatilization of potassium from the feldspar mixture is not as complete.

(2) As might be expected, no advantage is gained by the use of water vapor when there is present in the mixture sufficient chlorine as chloride to form with the potassium of the silicate the stable compound potassium chloride, whose vapor pressure, 101 mm. at 1215° C. and 202 mm. at 1300° C., is high enough to allow of rapid evaporation.

(3) The claims made by Spackman and Cornwell[1] that the presence of water vapor aids in the formation of potassium chloride from chlorides and potassium-bearing silicates appear to be unfounded.

VOLATILIZATION OF POTASH FROM LOW LIME SILICATE-CHLORIDE MIXTURES

In the previous experiments we had learned: first, that potash is volatilized at a lower temperature and more rapidly from greensand mixtures than from feldspar mixtures; and, second, that the volatilization of potash from low lime mixtures which fuse is slight. It was surmised, however, that in the latter case the low volatilization was due rather to the fusion of the mixture than to the lack of lime to set free the potash from the silicate.

A series of experiments was therefore run using mixtures of greensand with a chloride and with limestone in much smaller proportions than the proportion of

[1] *Loc. cit.*

limestone used in portland cement mixtures. In these experiments the mixtures given in Table VI were used.

TABLE VI—LOW LIME GREENSAND-CHLORIDE MIXTURES

Mixture No.	Materials Used	Proportions Grams	Ratio of Greensand / Limestone	Percentage of Chloride Added	Percentage of K_2O in Mixture
5	Greensand	50	1 : 1	None	3.85
	Limestone	50			
7	Greensand	10			
	Limestone	10	1 : 1	5.0	3.67
	Sodium chloride	1			
8	Greensand	10			
	Limestone	10	1 : 1	4.5	3.69
	Calcium chloride	0.9			
9	Greensand	20			
	Limestone	10	2 : 1	7.0	4.75
	Sodium chloride	2.1			
10	Greensand	20			
	Limestone	10	2 : 1	3.0	4.95
	Sodium chloride	0.9			

The results of heating these mixtures at temperatures just below those at which they start to fuse are given in Table VII.

TABLE VII—VOLATILIZATION OF POTASH FROM LOW LIME GREENSAND-CHLORIDE-LIMESTONE MIXTURES
(Air Passing at Rate of 100 to 150 Cc. per Min.)

Expt. No.	Mixture No.	Temperature °C.	Time, Min.	Ratio Greensand / Limestone	Chloride Kind	Chloride Per cent	Charge, G.	Loss in Wt. Per cent	Potassium Oxide In Charge Mg.	Potassium Oxide In Residue Mg.	Potassium Oxide Per cent Volatilized
155	5	1050	60	1:1	None		0.4419	25.12	17.0	17.2	0
161	5	1170	30	1:1	None		0.4810	25.63	18.5	17.3	6
163	5	1170	30	1:1	None		0.4641	25.45	17.9	16.9	6
156	7	1050	60	1:1	NaCl	5.0	0.4434	30.09	16.3	6.0	63
157	7	1190	15	1:1	NaCl	5.0	0.4862	31.96	17.8	0.4	98
158	7	1200	15	1:1	NaCl	5.0	0.4737	31.10	17.4	1.6	91
159	7	1170	15	1:1	NaCl	5.0	0.4627	31.55	17.0	1.6	91
165	8	1170	15	1:1	$CaCl_2$	4.5	0.4767	31.63	17.6	3.6	80
167	9	1170	15	2:1	NaCl	7.0	0.4222	28.00	20.0	3.0	85
171	10	1170	15	2:1	NaCl	3.0	0.4260	24.25	21.1	8.1	62

A consideration of the results given in Table VII shows that:

(1) The volatilization of potash from a 1:1 mixture of greensand and limestone without the addition of a chloride is very small at temperatures up to 1170° C. This is true even in the presence of water vapor which was used in Expt. 163.

(2) On addition of a chloride in proportion slightly greater than that calculated for the formation of potassium chloride, the potash in greensand and limestone mixtures can be readily volatilized at temperatures slightly lower than the temperatures at which the mixtures begin to fuse. This has been shown for mixtures containing as little as one-third limestone.

(3) Sodium chloride appears to be somewhat more efficient than calcium chloride as a volatilizing agent, and when less chloride is used than the amount calculated to give potassium chloride with all of the potassium in the mixture there is a decided decrease in the volatilization.

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